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An Empirical Model for Refrigerant Flammability Based on Molecular Structure and Thermodynamics

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ABSTRACT

Screening methods for refrigerant blend flammability using metrics that can be easily calculated are of great interest to the refrigerant industry. Existing flammability metrics such as heat of combustion are not adequate for hydrofluorocarbon blends. Alternative metrics are needed that can be used to assess the flammability of refrigerant blends without requiring time-consuming experimental measurements.

In this work we study the combination of the maximum adiabatic flame temperature and the fluorine-substitution ratio as metrics for characterizing the flammability of refrigerant blends. The combination of these metrics yields an estimate of the flammability class of refrigerants (both blends and pure fluids) containing hydrofluorocarbon and hydrocarbon components. The calculations of adiabatic flame temperature are carried out with the open-source chemical kinetics software package Cantera using a mechanism available in the literature.

1. INTRODUCTION

In the search for low-global-warming-potential (GWP) replacements for refrigerants, the common performance metrics of coefficient of performance (COP) and volumetric capacity (Q_{vol}) remain important for both pure fluids and blends. Rigorously determined values for the GWP have been determined for only about 100 compounds, but an estimation method suitable for screening purposes has been developed by Kazakov *et al.* (2012). Using these techniques, pure compounds have been screened for their potential suitability (McLinden *et al.*, 2017). Blends of existing or new compounds have also been identified and optimized (Bell *et al.*, 2018). In order to complete the screening or optimization, however, a metric for flammability is also required.

2. FLAMMABILITY METRICS

The flammability of a refrigerant is classified by ANSI/ASHRAE Standard 34 (ASHRAE, 2016) and ISO Standard 817 (ISO, 2014) based on its heat of combustion, lower flammability limit, and laminar burning velocity. The classes range from “1” (fluids exhibiting “no flame propagation”) to “3” (“higher flammability”)—fluids with a heat of combustion greater than 19 MJ/kg *or* a lower flammability limit less than 0.10 kg/m³. Fluids of “lower flammability” are assigned to class “2.” Class 2 fluids have a heat of combustion less than 19 MJ/kg *and* a lower flammability limit greater than 0.10 kg/m³. There is a further subclass “2L” for class 2 fluids that also meet the additional condition of a maximum burning velocity less than 10 cm/s. Flame propagation and the lower flammability limit are determined by the test method specified in ASTM E-681 (ASTM, 2015), with slight modifications.

Although the distinct flammability classes of 1, 2L, 2, and 3 might suggest that there is a clear boundary between “flammable” and “nonflammable” refrigerants, flammability is, in fact, a continuum (Williams, 1974). While methane, for example, is clearly flammable and carbon dioxide is clearly nonflammable, many other fluids are somewhere in between. What constitutes “flammable” is a function of the test method and test conditions. The ASTM E-681 test (as modified for refrigerants) is carried out in a 12 L glass flask with premixed fuel and air, with ignition provided by an electric spark. The criteria for “flame propagation” is that the flame move upwards and outwards from the spark, extend to the walls of the flask, and subtend an angle equal to or greater than 90°, as measured from the point of ignition. Thus, a refrigerant exhibiting a weak flame with a flame angle less than 90° in the E-681 test would

be considered “nonflammable” under ASHRAE Standard 34. The test conditions can also affect flame propagation. Higher temperatures will generally enhance a flame, and for highly fluorinated species, tests in humid air will enhance the flammability compared to tests in dry air (this point is discussed further in section 2.2).

Among the flammability criteria considered in the ASHRAE and ISO standards, only the heat of combustion is easily calculated, provided that enthalpies of formation are available for the refrigerant and combustion products and that the products of combustion can be determined. The flammability limits are dependent on the specifics of the test method and cannot presently be calculated from first principles, and they must be determined from experiments. The burning velocity can be calculated from first principles very accurately for some hydrocarbons (Egolfopoulos *et al.*, 2014). However, it has only recently been calculated for pure HFCs with air (*e.g.*, R-32 (Burgess Jr *et al.*, 2018); C₁ and C₂ HFCs (Linteris and Babushok, 2018)), and for blends of HFCs with hydrocarbons (Linteris, 1996; Linteris *et al.*, 1998; Linteris and Truett, 1996; Pagliaro *et al.*, 2016a; Pagliaro *et al.*, 2016b). For accurate predictions however, additional research is necessary to understand the important effects of flame stretch (Pagliaro and Linteris, 2016), radiation heat losses (Burrell *et al.*, 2018), and buoyancy (Takizawa *et al.*, 2013). Also, the calculation of the laminar burning velocity of HFC compounds in air requires a detailed kinetic mechanism, and while these are in active stages of development (Babushok and Linteris, 2017; Needham and Westmoreland, 2017; Papas *et al.*, 2017), more work is required (Linteris and Babushok, 2018). Thus, while work is proceeding to calculate burning velocity, presently it must be measured.

An easily computed estimate of flammability would speed industry’s screening for and optimization of new refrigerants and blends. General estimates of flammability have been made in previous work, including the very early estimates based on heat of combustion. The heat of combustion can be easily calculated, and has been used as a metric for flammability in refrigerant screening tests, but it is too crude a metric for marginally-flammable hydrofluorocarbon (HFC) compounds. A similar metric, the adiabatic flame temperature, has been used in previous work, and an extended version of that metric is used in the present work.

2.1 Adiabatic Flame Temperature

The adiabatic flame temperature (T_{ad}) is the temperature reached by a reacting mixture of fuel (*e.g.*, refrigerant) and oxidizer (*e.g.*, air) that undergoes an exothermic (heat-releasing) reaction to its most stable equilibrium products, under adiabatic conditions. Invoking the first and second laws of thermodynamics, this parameter is calculated for conditions of either constant enthalpy and constant pressure (*HP*) or conditions of constant internal energy and constant volume (*UV*). For flames in unconfined spaces, the constant *HP* calculation is more appropriate, while for pressure vessels, a constant *UV* calculation is used. Conceptually, the difference in the bond energy between the reactant and product species manifests itself as a temperature rise in the products. In the constant *HP* case, the *PV* work done by the expanding gases is also accounted for. Using the difference in the heats of formation of the products and reactants, and their gas-phase specific heats (C_p or C_v), one could, in principle, readily calculate the temperature rise in the products. The equilibrium composition is temperature dependent, however, and for combustion conditions a wide range of actual products (including radical species) is present in the final gases. Hence, in practice, automated numerical approaches (Goodwin *et al.*, 2016; Gordon, 1996; Lutz *et al.*, 1998) are used that are based on minimization of the Gibbs Free Energy (G) (Turns, 2000); these use standard combustion databases for the entropy and enthalpy as a function of temperature (Kee *et al.*, 1989; McBride *et al.*, 2002). In the present work we use Cantera (Goodwin *et al.* 2016), an open-source suite of object-oriented software tools for problems involving chemical kinetics, thermodynamics, and transport processes.

The adiabatic flame temperature has been used previously as a metric for flammability. The approach builds upon very early work using the heat of combustion. For example, Le Chatelier and Boudouard (1898) found that for typical hydrocarbons, flammability requires a heat of combustion above about 4.2 kJ/mol. Nonetheless, recent examination for HFCs has found that, while there is a trend of heat of combustion varying inversely with the lower flammability limit, this approach shows considerable scatter (Kazakov *et al.*, 2012). The use of adiabatic flame temperature is an improvement over heat of combustion. Burgess and Wheeler (1911) found that for a wide range of hydrocarbons, flammability requires T_{ad} above 1600 K, and White (1925), Zabetakis (1965), and Weinberg (1971) expanded upon this work to show that the effects of differing initial temperatures, as well as most inert diluents, can be explained by their influence on the T_{ad} .

2.2 Fluorine Substitution Ratio

Supplementing the adiabatic flame temperature, the present method adds a metric that can account for changes to the chemical mechanism with varying composition of the reactants. The high temperature requirement for flammability of hydrocarbons results from the radical chain-branching reaction $\bullet\text{H} + \text{O}_2 \rightarrow \bullet\text{H} + \bullet\text{OH}$, which although it has a high activation energy and requires a high temperature, greatly increases the concentration of the chain-carrying radicals ($\bullet\text{H}$, $\bullet\text{O}$, and $\bullet\text{OH}$), and is generally responsible for the rapid reaction in these systems. For systems with lowered chain-branching, for example hydrocarbons with halogens substituted for some of the hydrogens, a different, higher temperature is required for rapid reaction, and the activation energy is different. For HFCs, as the hydrogen-to-fluorine substitution (also known as fluorine loading) in the system increases, the importance of the normal hydrocarbon radical pool ($\bullet\text{H}$, $\bullet\text{O}$, and $\bullet\text{OH}$) decreases, and the importance of fluorinated radicals increases (Babushok *et al.*, 2012; Linteris and Babushok, 2018). This shift in the kinetic mechanism from one dominated by the typical hydrocarbon radical pool to one dominated by fluorinated-species radical attack can be captured via the molar ratio of F to H atoms in the reactants. A convenient parameter capturing this is the molar ratio of F atoms to the sum of F and H atoms $F/(F + H)$ in the reactants (the ratio F/H has also been used, but becomes infinite for perfluorinated compounds). Typically, all sources of hydrogen in these systems react rapidly, and have the net effect of increasing hydrogen-containing radical species (*e.g.*, $\bullet\text{H}$ or $\bullet\text{OH}$) in the flame. Thus, added water vapor can increase the overall reaction rate by creating $\bullet\text{H}$ atoms and increasing the importance of the usual chain-branching reactions (Takahashi *et al.*, 2015; Takahashi *et al.*, 2017).

The importance of the F to H ratio to the flame reaction pathways has been shown in many works. Linteris (1994), Nyden *et al.* (1994), and Linteris and Gmurczyk (1995) studied HF formation in premixed and diffusion flames inhibited by HFCs and showed that the equilibrium products and flame kinetics change dramatically as F/H increases above unity ($F/(F + H) > 0.5$), and that premixed flame stability is markedly decreased for F/H near unity (Linteris and Gmurczyk, 1995). For methane-air and propane-air systems with added R-32, R-125, R-227ea, or R-116, premixed flames (*i.e.*, those resulting from premixed reactants) could not be stabilized for values of F/H greater than unity (Linteris and Gmurczyk, 1995). In experimental studies of burning velocity of various pure HFC compounds in moist and dry air (Linteris, 1999), the F/H ratio was found to be a key parameter determining flame stability and burning velocity, and highlighted the importance of water vapor in the air. Similarly, in experimental studies with premixed flames of R-32, R-143, R-143a, or R-152a with air, Takizawa *et al.* (2005) found the burning velocity to drop off rapidly as $F/(F + H)$ increased above 0.5. In numerical premixed flames simulations employing detailed kinetic mechanisms (Linteris and Babushok, 2018), calculated burning velocities were also found to drop rapidly as $F/(F + H)$ approached and exceeded 0.5, where the fundamental reaction kinetics shifted from typical hydrocarbon radical pool species ($\bullet\text{H}$, $\bullet\text{O}$, and $\bullet\text{OH}$) to fluorinated species. Hence, the parameter $F/(F + H)$ is expected to be useful for describing the shift in kinetics and changes to flame stability for refrigerant blends.

3. CALCULATION OF ADIABATIC FLAME TEMPERATURE

For the calculation of the adiabatic flame temperature, the initial reaction mixture is given by:

$$\phi \cdot \text{Fuel} + \Gamma \left[\text{O}_2 + 3.76 \text{N}_2 + \frac{X_{\text{H}_2\text{O}}}{\left(\frac{1.0}{4.76}\right)(1-X_{\text{H}_2\text{O}})} \text{H}_2\text{O} \right] \quad (1)$$

in which ϕ is the fuel-air equivalence ratio, and has a value of <1 for lean combustion, >1 for rich combustion, and 1 for stoichiometric combustion. The fuel is given by the sum of the molar fractions x_i of its constituent refrigerants (i), and Γ is the molar oxygen requirement for stoichiometric ($\phi=1.0$) combustion of one mole of fuel (refrigerant blend). The nitrogen in the air is relatively inert in the combustion reactions, although it does absorb heat because some of the heat of reaction goes to heating the nitrogen to T_{ad} .

The water vapor volume fraction in the oxidizer (air) is denoted $X_{\text{H}_2\text{O}}$. The air is modelled as having an $\text{N}_2:\text{O}_2$ ratio of 3.76:1.0 such that the molar composition of the humid air is:

$$\text{N}_2: (3.76/4.76)(1 - X_{\text{H}_2\text{O}}),$$

$$\text{O}_2: (1.0/4.76)(1-X_{\text{H}_2\text{O}}),$$

$$\text{H}_2\text{O}: X_{\text{H}_2\text{O}}$$

These conditions correspond to a dry air O_2 volume fraction of 0.21. The volume fraction of water vapor $X_{\text{H}_2\text{O}}$ is selected to be 0.014, corresponding to air at 23 °C and 50 % relative humidity in accordance with the flammability tests specified in ASHRAE Standard 34.

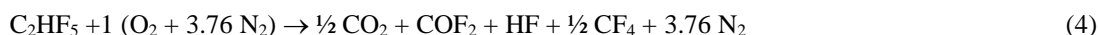
Γ is approximated as the mole-fraction-weighted average of the individual stoichiometric air requirements for each constituent ν_i ,

$$\Gamma = \sum_{i=1}^{N_{\text{comp}}} x_i \nu_i \quad (2)$$

The value of ν_i for a given pure compound is determined by conducting an equilibrium calculation (constant enthalpy and pressure) for a range of fuel-air ratios, and then examining the equilibrium products. From these, it is possible to write a stoichiometric reaction with appropriate coefficients. For example, for R-134a ($\text{C}_2\text{H}_2\text{F}_4$), the equilibrium products indicate an approximate stoichiometric reaction given by:



such that $\nu_i = 1.5$ for R-134a. Similarly, for R-125, the stoichiometric reaction is:



and $\nu_i = 1.0$ for R-125. The values of ν_i are listed in Table 1 for stoichiometric combustion. For hydrocarbons, $\nu_i = n_{\text{C}} + n_{\text{H}}/4$, in which n_{C} is the number of carbon atoms in the fuel molecule, and n_{H} is the number of hydrogen atoms.

The value of Γ given by Eq. (2) is an initial estimate, as it can vary with the reactants. For example, while the combustion of R-134a with air yields COF_2 as one of the products, a mixture of R-134a and propane may not. This is because some of the hydrogen atoms from the propane (that would have formed H_2O) can react with the fluorine atoms from the R-134a to give HF in preference to COF_2 . The final set of combustion products for the given reactants is one of the key outputs from the Cantera equilibrium calculations.

For the final determination of T_{ad} for a given “fuel”, the equilibrium calculation is performed again for the estimated value of Γ , over a range of $0.5 \leq \phi \leq 2.0$ in Eq. [1], and the peak value of T_{ad} is selected. This value of ϕ for the peak value is typically within a few percent of $\phi = 1.0$, validating the approximation of Γ as a mole-fraction-weighted combination of the individual ν_i . Note also that while the estimation of ν_i and Γ are based on dry air, the final estimates of $F/(F+H)$ and T_{ad} are based on moist air as specified in ASHRAE Standard 34. Since the final T_{ad} are determined as the peak value over a range of ϕ , any variation in ν_i and Γ due to the presence of the moisture in the air is accounted for in the final value of peak T_{ad} .

As Table 1 shows, the flammable HFCs have T_{ad} close to those of hydrocarbons, and as the fluorine loading increases, T_{ad} decreases mildly and then more strongly as $F/(F+H)$ increases above 0.5. For T_{ad} near 2000 K, values of $F/(F+H)$ of about 0.66 denote the boundary between flammable and non-flammable (for these compounds).

It is worth commenting on values of T_{ad} as high as 1928 K among the “nonflammable” refrigerants listed in Table 1; indeed, what does a “flame temperature” mean for a nonflammable fluid? This has to do with reaction kinetics (*i.e.*, the rate of chemical reaction). The concept of the adiabatic flame temperature is based on equilibrium thermodynamics for an adiabatic system (infinite time, zero heat losses). Hence, while the equilibrium products of R-134a in the presence of air are CO_2 , HF, and COF_2 , at $T_{\text{ad}} = 1940$ K, as indicated by Eq.(3), this state is typically not reached under normal conditions because the reaction kinetics are too slow; *i.e.*, R-134a in air is “nonflammable” because the reaction rates are too slow.

Table 1: Properties of selected pure refrigerants in ASHRAE Standard 34. The adiabatic flame temperature T_{ad} and $F/(F + H)$ are based upon a volume fraction of H_2O in the air of 0.014, and the initial temperature is 296.15 K.

Refrigerant (<i>i</i>)	Formula	γ_i	$F/(F + H)$	T_{ad} (K)	\bar{P}
<u>A3, Flammable</u>					
R-290	C_3H_8	5	0.000	2262	100
R-1270	C_3H_6	4.5	0.000	2338	100
R-600	C_4H_{10}	6.5	0.000	2265	100
R-600a	iso- C_4H_{10}	6.5	0.000	2261	100
R-601	C_5H_{12}	8	0.000	2265	100
R-601a	iso- C_5H_{12}	8	0.000	2265	100
<u>A2, Flammable</u>					
R-152a	CH_3-CHF_2	2.5	0.316	2208	55.8
<u>A2L, Mildly flammable</u>					
R-32	CH_2F_2	1	0.484	2190	35.6
R-143a	CH_3-CF_3	1.5	0.479	2100	28.3
R-1234yf	$CH_2=CF_2$	2.5	0.633	2046	6.9
R-1234ze(E)	$CFH=CHCF_3$	2.5	0.633	2046	6.9
<u>A1, Nonflammable</u>					
R-134a	CH_2F-CF_3	1.5	0.645	1928	-8.1
R-125	CHF_2-CF_3	1	0.815	1788	-34.7
R-227ea	C_3HF_7	1.5	0.853	1791	-35.5
R-218	C_3F_8	1	0.983	1581	-62.4
R-744	CO_2	n.a.	n.a.	n.a.	n.a.

4. RESULTS—ESTIMATION OF FLAMMABILITY

The present approach calculates, for a given set of premixed reactants, the adiabatic flame temperature T_{ad} and the fluorine loading, expressed as $F/(F + H)$. The existing ASHRAE Standard 34 flammability designations are then used to produce a map of the flammability as a function of T_{ad} and $F/(F + H)$. The dataset included in this comparison are mixtures of the pure compounds listed in Table 1. The pure compounds include: flammable (class 3) hydrocarbons; flammable (class 2) R-152a; mildly flammable (class 2L) HFCs and hydrofluoroolefins (HFOs), and the nonflammable (class 1) HFCs and CO_2 .

Figure 1(a) shows the T_{ad} and $F/(F + H)$ values for each of the refrigerants listed in ASHRAE Standard 34 which contain the compounds in Table 1 at various compositions. The pure compounds are shown as closed circles, and the blends, open circles. The dotted lines were manually drawn to separate the different flammability regions. The origin of those lines is at $T_{ad} = 1600$ K and $F/(F + H) = 0$. This point corresponds to hydrocarbons at their flammability limit, which is appropriate, since as described above, 1600 K is an empirically observed flammability limit for hydrocarbon flames over a wide range of hydrocarbons, inert diluents, and flame configurations.

We define a “flammability index” II based on the angle that a point in $[F/(F + H), T_{ad}]$ coordinates makes with the origin point at (0, 1600 K), in which the temperature difference ($T_{ad} - 1600$ K) is normalized by a reasonable upper-limit T_{ad} , which we select to be 2500 K:

$$\Pi = \arctan2 \left\{ \left[\frac{T_{ad} - 1600}{(2500 - 1600)} \right], \left[\frac{F}{(F+H)} \right] \right\} \cdot \left(\frac{180}{\pi} \right), \quad (5)$$

where $\arctan2(y, x)$ gives the four-quadrant arctangent angle in the domain $[-\pi, \pi]$, and the angle is then shifted to the domain $[-180^\circ, 180^\circ]$. A normalized flammability index $\bar{\Pi}$ is then defined by

$$\bar{\Pi} = \frac{\Pi - \Pi_{1,2L}}{90 - \Pi_{1,2L}} \cdot 100, \quad (6)$$

with $\Pi_{1,2L}$ is equal to 34.78. This results in a normalized flammability index which is zero at the 1/2L boundary and 100 for the highly flammable hydrocarbons. Values less than zero indicate that the mixture is probably nonflammable according to the ASHRAE Standard 34 criteria.

The blends shown in Figure 1(a) are calculated for the compositions listed in ASHRAE Standard 34—the so-called “nominal” compositions. In fact, the flammability classification of blends is based on a slightly different composition. Standard 34 specifies a composition tolerance for each component in a blend to account for variations in blending by the refrigerant producer. The “most flammable” composition resulting from a blend at the extreme of the tolerances is denoted as the “worst case of formulation for flammability” (WCF). This WCF composition is then analyzed for possible composition shifts resulting from defined leakage scenarios, yielding a “worst case of fractionation for flammability” (WCFF). The flammability testing of blends is then carried out at the WCF and WCFF compositions. Sometimes, for multicomponent blends, multiple possible WCF and WCFF compositions are tested to determine the worst case. We extracted the flammability test data from the applications to the Standard 34 committee for new refrigerant designations. The flammability test data in each application at those WCF and WCFF compositions are plotted as a function of T_{ad} and $F/(F + H)$ in Fig. 1(b). This was done for the applications submitted for R-444A through R-462A (corresponding to applications submitted from 2012 to 2016). As per the ASTM E-681 test method, we classify the flammability of the mixture based on the maximum flame angle observed in the test; maximum flame angles $> 90^\circ$ are “flammable” and those $< 90^\circ$ are “nonflammable.”

The overall results from the WCF and WCFF compositions are substantially the same as those from the nominal compositions, and the resulting boundary between class 1 and class 2L is essentially the same. There is more scatter seen with the WCF and WCFF compositions, and we drew the boundary to be conservative. The flammability data from the applications is particularly valuable in defining the 1/2L boundary because many of the blends were formulated to be close to the boundary. For example, some blends include a hydrocarbon to improve oil solubility characteristics; a higher concentration of hydrocarbon would be advantageous for the oil solubility, and it would be set as high as possible without crossing into the flammable region.

As indicated, the parameters adopted provide a reasonable estimate of the flammability for these compounds evaluated via the ASHRAE criteria. Moreover, the slope of the line between that data point and the origin ($F/(F + H) = 0$, $T_{ad} = 1600$ K), *i.e.*, the flammability index defined above, can provide a relative measure of the flammability of a refrigerant. Such an approach can provide a first estimate of the flammability of a new blend, which increases as the slope increases. This method of flammability estimation has been used in the screening work described in Bell *et al.* (2018).

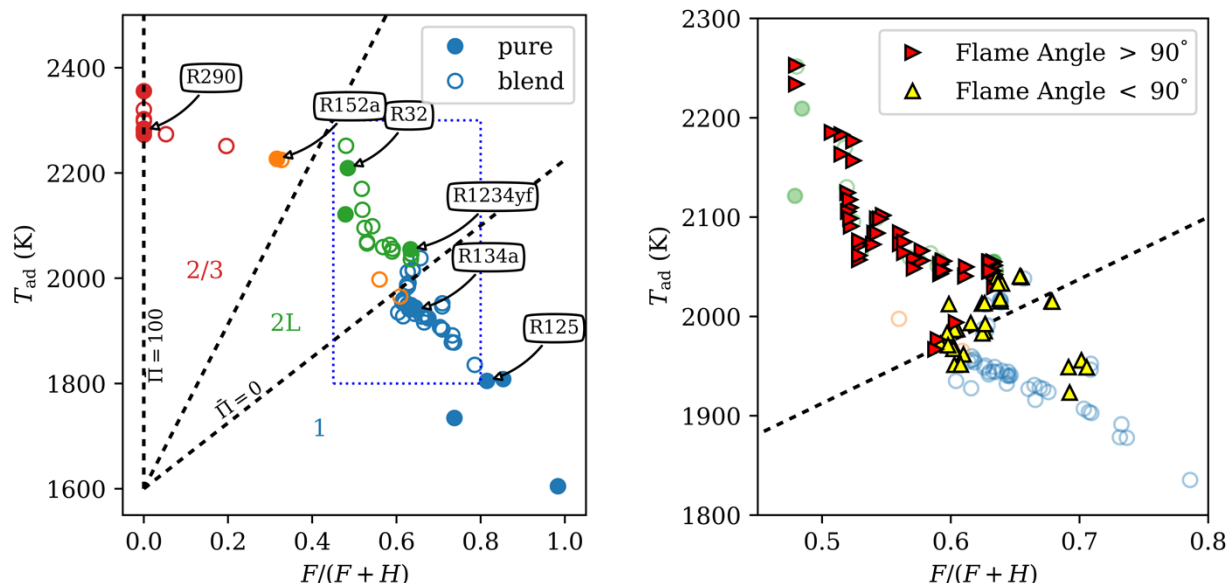


Figure 1: ASHRAE Standard 34 flammability classification (A1, A2L, A2, or A3) shown as a function of T_{ad} and $F/(F+H)$ for blends (open circles) and pure compounds (closed circles). The pure compounds are listed in Table 1. (a) ASHRAE Standard 34 flammability rating (1: blue, 2L: green, 2: orange, 3: red); (b) inset with measured flame angles for WCF and WCFE compositions from ASHRAE 34 applications (where available).

5. CONCLUSIONS

The present empirical estimate for the flammability of hydrofluorocarbon refrigerants is based on historical work showing the influence of the adiabatic flame temperature on hydrocarbon flammability limits, and the influence of fluorine-containing species on the combustion chemistry of hydrocarbon flames. These two effects are described by T_{ad} and the fluorine loading in the refrigerant, expressed as the molar ratio of F to (F + H) in the reactants. The adiabatic flame temperature is determined, using the Cantera open-source kinetics solver, as the peak value over a range of fuel-air ratios for the given refrigerant (pure compound or blend) in moist air at 296 K.

Using the ASHRAE flammability designations, a map of T_{ad} vs. $F/(F+H)$ is developed showing the regions of these parameters corresponding the flammable (A2 and A3), mildly flammable (A2L), and nonflammable (A1) regions. A metric is developed based on these parameters to rank the flammability (according to the ASHRAE Standard 34 criteria) for an arbitrary blend of constituents for which the chemical composition is known, and the adiabatic flame temperature can be calculated. The agreement with the existing data in the ASHRAE Standard 34 refrigerant database is good.

It should be noted that the present flammability ranking system is based on the ASHRAE Standard 34 test methods. For flammability configurations that require a different (*i.e.*, more or less stringent) flammability requirement, the present method may not be accurate. Also, for application to new compounds or blends, it is required that the new constituent compounds for which T_{ad} and $F/(F+H)$ are to be calculated are chemically similar to the compounds used to develop the model.

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